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Proportional Counter Designed for Resonance-Electron Mössbauer Spectroscopy

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Performance of our proportional counter recently improved for the ^{57}Fe resonance-electron Mössbauer spectroscopy is described in detail.

KEY WORDS: Proportional Counter/Mössbauer Spectroscopy/Resonance Electron/CEMS/REMS/

1. INTRODUCTION

An electron detector for the cryogenic resonance-electron Mössbauer spectroscopy (REMS), i. e., helium-filled proportional counter, was developed in a series of studies on the operation of proportional counter at low temperatures (2～77 K)[1~3]. The proportional counter is useful also at higher temperatures (77～300 K) as long as He+2%CH_4 or He+10%CO is filled instead of pure helium. We have found that the proportional counter recently improved is more efficient for electron detection than any counters previously developed for REMS measurements at higher temperatures[4~6]. In this article, we report the performance of our most favourite counter for ^{57}Fe REMS at high temperatures (77～300 K).

2. RESONANT AND NON-RESONANT ELECTRONS

In the ^{57}Fe REMS, electrons emitted after the nuclear resonance absorption of incident 14.4-keV γ rays in a sample contribute to the resonance peak of Mössbauer spectra. Those electrons consist of conversion electrons and Auger electrons; conversion electrons are emitted through the de-excitation of the 14.4-keV level resonantly excited by incident 14.4-keV γ rays and Auger electrons are emitted through the de-excitation of the atomic hole states created by the conversion process. The relative intensities of the resonant electrons are 79% per resonance for K conversion (7.3 keV), 8% for L conversion (14.3 keV) and 56% for KLL and KLM Auger processes.

The background counts in the Mössbauer spectra mainly comes from electrons produced by the interaction of incident photons with the sample and other counter materials. Incident photons from Mössbauer source consist of 14.4-keV γ rays (8.4%),

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122-keV γ rays (85%) and 136-keV γ rays (11%), and Fe K X rays (52%); the values in the parenthesis indicate the relative intensities per decay of ^{57}Co. X rays from matrix metal of ^{57}Co source is not negligible, e. g., 8.1-keV Cu K X rays and 20.2-keV Rh K X rays. 14.4-keV γ rays and K X rays effectively produces low-energy electrons through the photo-effect with sample or other counter materials. 122-keV and 136-keV γ rays produce high-energy electrons through the photo-effect and the Compton effect; with these γ-ray energies, the photo-effect becomes dominant for high-Z elements, e. g., Pb and Au, while the Compton effect becomes dominant for rather low-Z elements, e. g., Al and Ti. The electron production probability of those high-energy γ rays is much less than that of 14.4-keV γ rays and K X rays because of their relatively small absorption coefficients.

Both the low-energy and high-energy electrons, which are not connected to the nuclear resonance absorption of 14.4-keV γ rays, contribute to background counts of the Mössbauer spectrum. In order to obtain Mössbauer spectra with effects as high as possible, it is necessary to suppress the creation of such non-resonant electrons in the electron detector and also to employ the detector less sensitive to non-resonant electrons with high-energies.

3. DESIGN OF COUNTER

In REMS measurements, samples are mounted inside a counter to detect electrons emitted from them; the sample forms a part of cathode and is irradiated by incident beam of γ rays from the Mössbauer source. Gas-filled proportional counters are usually used to detect electrons in the ^{57}Fe REMS. To design a proportional counter efficient for the electron detection, the followings are to be considered.

1) Filling gases: Gases less sensitive to incident photons is to be employed. The Q gas, i. e., He+2%C_4H_{10}, which is commercially available, is often employed as the filling gas. At low temperatures near liquid nitrogen temperature (77 K), this gas mixture is not available because of the liquefaction of isobutane. A gas mixture of He+2%CH_4 or He+10%CO is used in our measurements at low temperatures near 77 K; the presuure of filling gas is usually 760 Torr at room temperature (RT)[6]. Pure helium gas is available near liquid-helium temperature (4.2 K)[1-3].

2) Materials: To suppress the creation of non-resonant electrons, materials composed of lower Z elements are to be employed for counter frames and entrance window. Aluminum or Lucite covered with an evapolated aluminum layer were used in our previous works.

3) Absorbers: Fe K X rays produce non-resonant electrons (photo-electrons) most effectively in incident photons from the ^{57}Co Mössbauer source. Lucite or aluminum is usually used as an absorber to diminish those X rays; high-Z materials are not available because of high absorption of 14.4-keV γ rays. The effciency to penetrate 1-mm thich Lucite is 19% for 6.4-keV Fe K X rays and 85% for 14.4-keV γ rays and that to penetrate 50-μm thick aluminum foil is 26% for the X rays and 87% for the γ rays.

4) Collimation: A careful beam alignment is necessary to make the incident

photons collide at the center of samples, which forms a part of cathode. A thin lead plate (1~2cm) is usually used to collimate the incident photons; the efficiency to penetrate 1-mm thick lead plate is 1.1% for 122-keV γ rays.

5) **Density of filling gas**: To obtain a good energy resolution for resonant electrons (at most 15 keV), the thickness of gas layer is to be more than the range of 15-keV electrons, which is about 29mm for helium with a pressure of 760 Torr at RT. Non-resonant electrons with high energies (about 100 keV) deposit only a part of their energies in the gas layer. The absorbed energy depends on the density (or pressure at a constant temperature) in the gas layer. The background count of Mössbauer spectra increases with increasing gas density. Thus, it is diffcult to decrease the background counts keeping the energy resolution good. The energy resolution and the background as a function of the gas density have been examined, as explained later.

4. COUNTER

4.1 Counter Geometry

Layouts of two proportional counters are given by Fig. 1. The counter A is the same as that used for cryogenic REMS measurements, in which the filling gas can be sealed[3]. The counter B is of gas-flow type, which is exclusively used at RT. The anode wire of both counters is 30-μm-diam. gold-coated tungsten wire. The frame is made of an aluminum block, of which thickness is 1.5cm for the counter A and 1.0cm for the counter B. The sensitive area of the counter A is considerably larger than that of the counter B: A, 4-cm diam. ×1.5-cm thick; B, 2.5-cm daim. ×1-cm thick. The both counters are much larger than counters used in our previous works, typically 1.6×1.6cm^2 ×3mm thick[3,4]. The cathode is formed by the counter frame, a 30-μm thick aluminum film attached on the Lucite absorber and a sample mounted on the opposite side of the absorber. To irradiate the sample without colliding wall materials, inci-

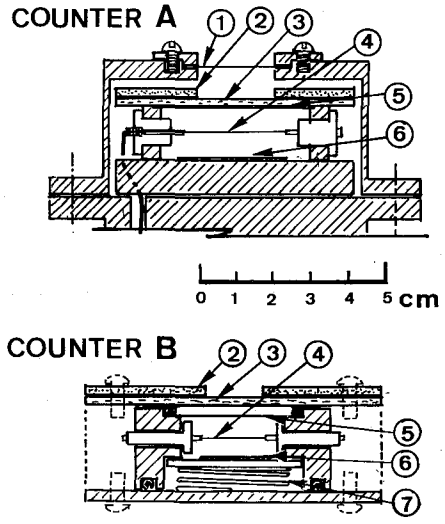

Fig. 1. Layouts of two proportional counters examined: 1, entrance window (100-μm thick aluminum); 2, lead collimater; 3, Lucite absorber; 4, anode wire (30-μm diam. gold-coated tungsten wire); 5, 30-μm thick aluminum cathode; 6, sample; 7, spring. The counter A is designed for cryogenic REMS measurements while the counter B or gas-flow type is exclusively used at room temperature.

dent radiations are collimated by a lead plate with a hole, of which diameter is 2.0cm for the counter A and 1.5cm for the counter B. A part of incident photons are absorbed by materials in the path of photons, that is a 100-μm thick aluminum window, a 2-mm thick Lucite absorber and a 30-μm thick aluminum cathode for the counter A and a 3-mm thick Lucite absorber and a 30-μm aluminum cathode for counter B. The penetration of photons through the counter A is 0.1% for 6.4-keV Fe K rays and 50% for 14.4-keV γ rays. The efficiency of the counter B is 0.3% for the X rays and 56% for the γ rays.

A gas mixture of He+2%CH_4 has been employed in the present work. The absorptions of 6.4-keV and 122-keV photons in 1-cm thick He+2%CH_4 layer (760 Torr at RT) are 0.09% and 0.018%, respectively. Counts caused by the absoption of incident photons contribute to the background of Mössbauer spectra; its contribution is probably much smaller than that of the non-resonant electrons from the sample.

4.2 Energy Resolution

A thin electron source (~1.0 kBq) has been prepared by electroplating ^{57}Co on a 20-μm thick aluminum foil. The source is mounted at the cathode of the counters to detect directly low-energy electrons emitted from the source. Typical energy spectra of the low-energy electrons measured with the counters A and B are given by Fig. 2 (a) and (b), respectively. The filling gas is He+2%CH_4 with a pressure of 760 Torr at

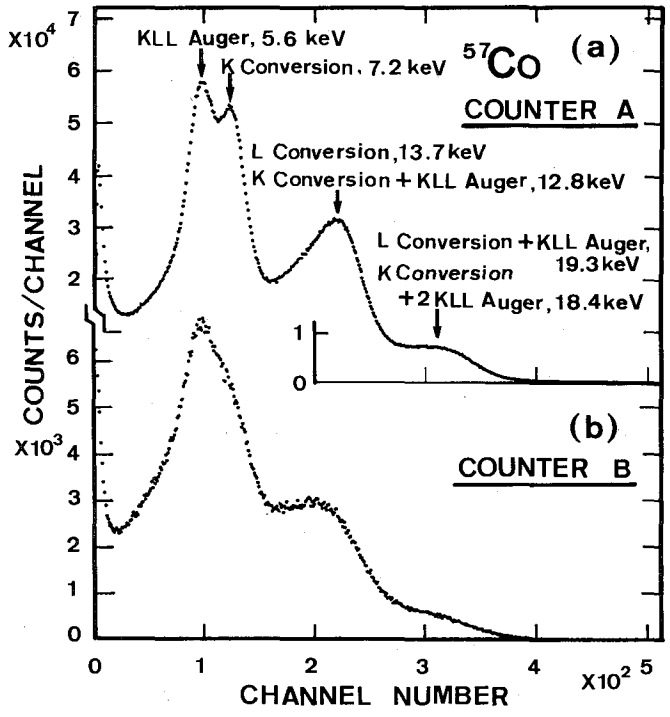

Fig. 2. Energy spectra of electrons emitted from a ^{57}Co source: (a), with the counter A; (b), with the counter B. The counter gas is He+2%CH_4 (760 Torr at RT).

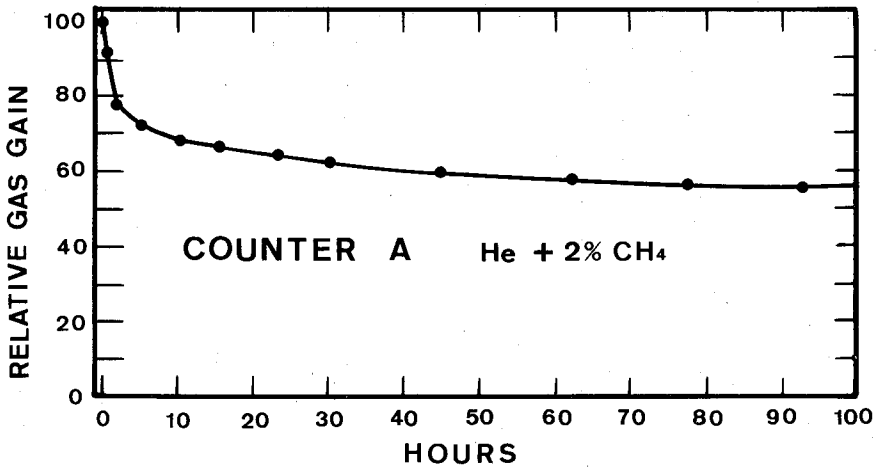

Fig. 3. Drift of gas gain of the counter A of gas-seal type. The counter gas is He+ 2%CH_4 (760 Torr at RT).

RT. The layer of this gas mixture (1.5cm for the counter A and 1.0cm for the counter B) is enough thick to absorb whole energies of the resonant electrons (at most 15keV).

As seen in Fig. 3, the energy resolution of the counter A is better than that of the counter B. The distortion of the electric field in the counter, specially near anode wire, always results in making the energy resolution worse. The counter A is so large that most of low-energy electrons emitted from the source can lose their whole energies in the central region of the counter, of which electric field is approximately uniform. On the other hand, the counter B is not large enough to obtain a region with uniform electric field.

4.3 Gain drift

Gas gain of mixtures, He/CH_4 and He/CO, was measured in our previous work[7,8]. Available gas gain of these mixtures approahes to 10^4. When the counter gas is flowed through the counter, the drift of gas gain is not so large to disturb REMS measurements. When the counter gas is sealed in the counter, the gas gain gradually decreases.

A gain drift of the counter A is shown in Fig. 3; the filling gas is He+2%CH_4 (760 Torr at RT) and the gas gain is about 10^3. After the counter gas is filled, the gain steeply decreases to 75% in two hours. Then, the gain decrease becomes gradual with hours. Long-run measurements (longer than a week) are actually possible for the period about one day later after the gas filling; the gain decrease in this period is below 20%.

Since the ionization potential of helium is highest in all gases, helium is most sensitive to the amount of impurity gases; ionization processes in helium is greatly affected by a small amount of impurities[2]. The gas mixture of He+2%CH_4 is also sensitive to impurities such as outer gases coming from surrounding materials. The decrease of gain shown by Fig. 3 is probably caused by the outer gases. Possible emitters of outer gases in the counter A are the Lucite absorber and solders to fix the

anode wire. It is possible to suppress the gain decrease below 5%, if the counter is constructed with Teflon, stainless steel and cupper and carefully rinsed with available solvents[9].

The gain drift at low temperatures near 77K is similar to that shown in Fig. 3. Recently, a systematic study of gain drift of some helium gas mixtures at 77 and 300K has been performed by Fukumura et. al[10].

5. S/N RATIO OF MÖSSBAUER SPECTRA

5.1 S/N ratio

Mössbauer spectra measured for a stainless steel (304) at RT are shown in Fig. 4: (a), with the counter A; (b), with the counter B. The counter gas is He+2%CH_4 with a pressure ot 760 Torr at RT. The discriminator to cut off electric singnals from the counters was set just above the noise level. Both spectra have almost the same effect with a 100% baseline, i. e., ~10%. In the measurements, incident photons from the ^{57}Co Mössbauer source are carefully collimated not to collide with counter wall. When the collimation of the incident beam was not sufficient, the S/N ratio was

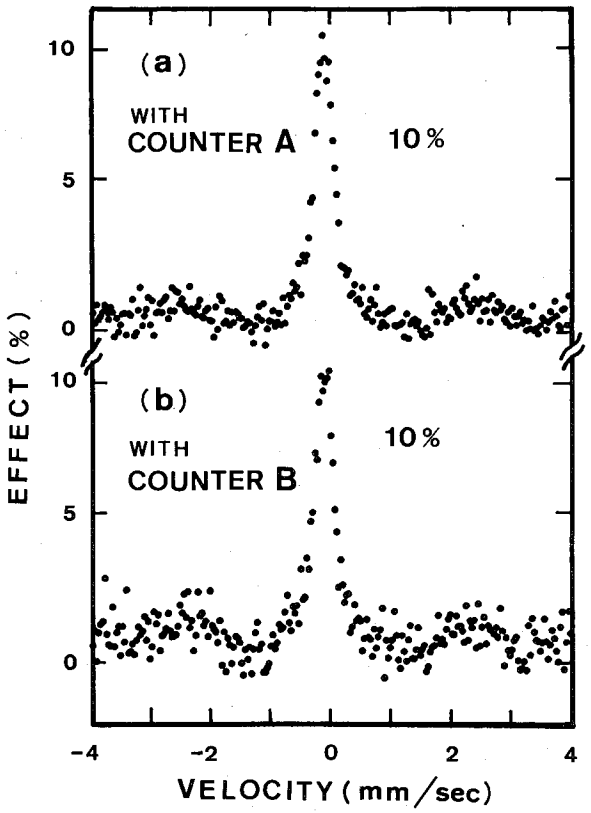

Fig. 4. Mössbauer spectra measured for a stainless steel (304) at RT: (a), with the counter A; (b), with the counter B. The counter gas is He+2%CH_4 (760 Torr at RT).

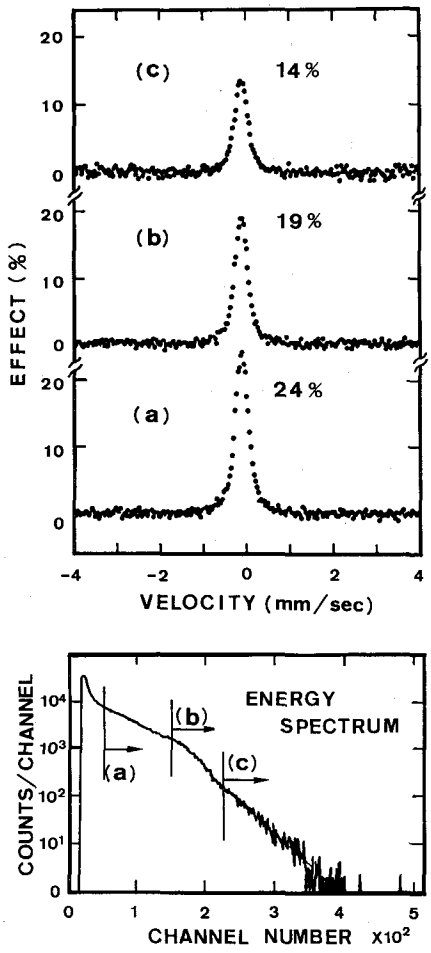

Fig. 5. Energy spectra of electrons in REMS measurements and Mössbauer spectra corresponding to various regions of electron energy; Mössbauer spectra (a), (b), and (c) corresponds to the lower discriminator setting at the level (a), (b) and (c) in the energy spectrum, respectively. The sample is a stainless steel of Type 310. Those spectra were obtained with the counter A filled with He+2%CH_4 (760 Torr at RT).

always worse than that of the spectra in Fig. 4.

The energy spectrum of electrons in the REMS measurement, which are emitted from the sample mounted inside the counter (A), is shown by Fig. 5; the sample is a stainless steel of Type 310. In the figure are also shown Mössbauer spectra obtained for three regions in the energy spectrum. As the setting of the lower discriminator is higher, the S/N ratio of Mössbauer spectrum becomes worse. This result is different from that obtained with the previous small counter (250mm² ×3mm);[4] the S/N ratio was better with a higher discrimator setting. This probably comes from a difference in energy resolutions of the two counters; the resolution of the previous counter is much worse than that of the counter A.

5.2 Mesh For Non-Conducting Samples

A difficulty in the REMS measurement for non-conducting materials is the charging up of cathode. When electric charges are accumulating on a non-conducting sample as cathode, the height of output signals from the counter becomes lower because of the gradual increase of earth potential. To avoid this effect, the sample is

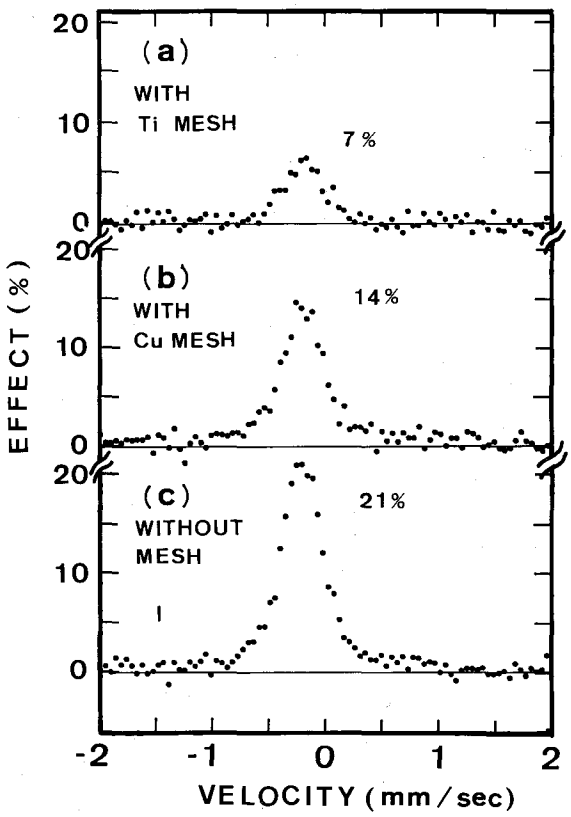

Fig. 6. Mössbauer spectra obtained with and without metal meshes; (a), with titunium mesh (0.2-mm diam., 1.5-mm space); (b), with cupper mesh (50-μm diam., 2-mm space); (c), without mesh. The sample is a stainless steel of Type 310.

covered with a metal mesh. A rather large mesh is enough for the REMS measurements; we usually wind a fine cupper wire (50-μm diam.) around the non-conducting sample with the space of 3~5mm. With such a large mesh, we succeeded to obtain Mössbauer spectra of Fe_3O_4 epitaxial films[11-12] and a single crystalline $Bi_3Fe_5O_{12}$ at low temperatures near 4.2K[13].

In Fig. 6 are shown Mössbauer spectra of a stainless steel of Type 310 covered with and without metal meshes: (a), with titanium mesh (0.2-mm diam., 1.5-mm space); (b), with our method of winding cupper wire (50-μm diam. 2-mm space); (c), without mesh. The S/N ratio of Mössbauer spectrum obtained without mesh is 21% while that obtained with the cupper winding is 14%. The decrease of this order is permittable in most of REMS measurements.

5.3 Background Counts

The relative intensity of non-resonant electron as a function of gas density has been approximately determined in the present work. In Fig. 7 are shown the spectra of signals from the counter A, in which a thin ^{57}Co source electroplated on a aluminum

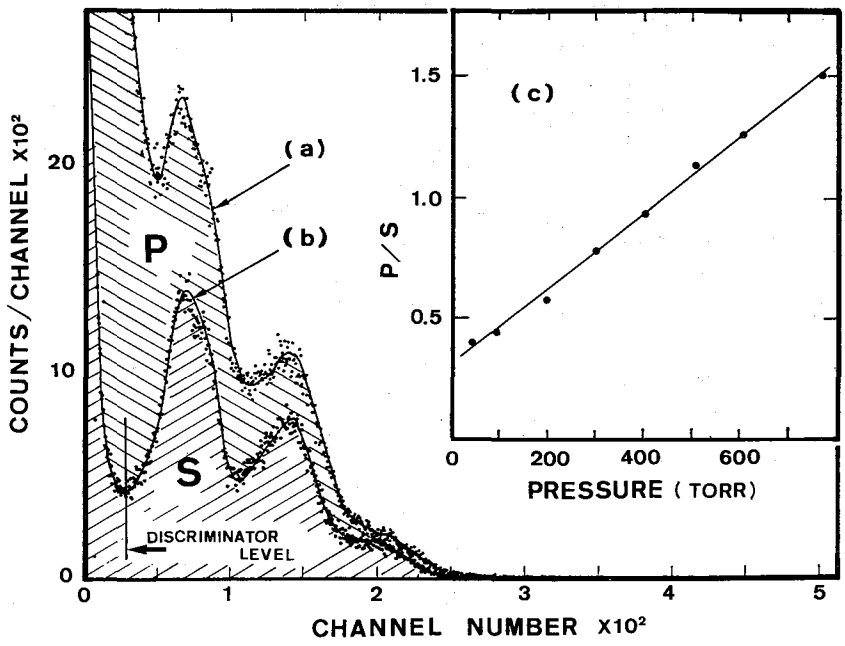

Fig. 7. One of energy spectra of electrons from the internal ^{57}Co source (~1.0 KBq) for determining the relative intensity of non-resonant electrons: (a), with the irradiation by incident photons from the external ^{57}Co Mössbauer source (~1.8 GBq); (b) without the irradiation. The counter gas is $He+2\%CH_4$, of which pressure is changed from 50 Torr to 760 Torr at liquid nitrogen temperature (77 K). The curve (c) gives the relative intensity of non-resonant electrons as a function of the pressure of counter gas.

foil is mounted: the spectrum (a) is obtained by irradiating the counter with photons from a ^{57}Co Mössbauer source (~1.8 GBq) while the spectrum (b) is obtained without the irradiation. The counter was cooled at liquid-nitrogen temperature (77 K) to fill the counter gas ($He+2\%CH_4$) at high gas density. The pressure of the counter gas was changed from 50 Torr to 760 Torr at 77 K. The ratio of non-resonant electrons (indicated by P in the figure) to electrons from the internal source (indicated by S) is plotted as a function of the pressure of the counter gas, as shown by the curve (c) in Fig. 7. The P/S ratio increases with increasing pressure, as expected.

Mössbauer spectra of a stainless steel of Type 310 measured with the gas pressures of 60 Torr, 200 Torr and 600 Torr are shown in Fig. 8 (a), (b) and (c), respectively; measurements were performed at 77 K. The best S/N ratio of the Mössbauer spectrum is 49% at a pressure of 60 Torr; however, the energy resolution is apparently worse than that obtained with the pressure higher than 200 Torr. The S/N ratio at 600 Torr is 29%. The counting effciency for non-resonant electrons enhanced at higher gas pressure results in the decrease of the S/N ratio, as discussed above. The difference of S/N ratios at 60 Torr and 200 Torr is rather small while the energy resolution at 200 Torr is sufficieltly good. The pressure of 200 Torr at 77 K corresponds to 770 Torr at RT. The present result indicates that the gas density usually employed, i. e., 760 Torr at RT, is reasonable to obtain both a good energy resolution and high S/N ratio for the counter with a 1~1.5-cm thick helium layer.

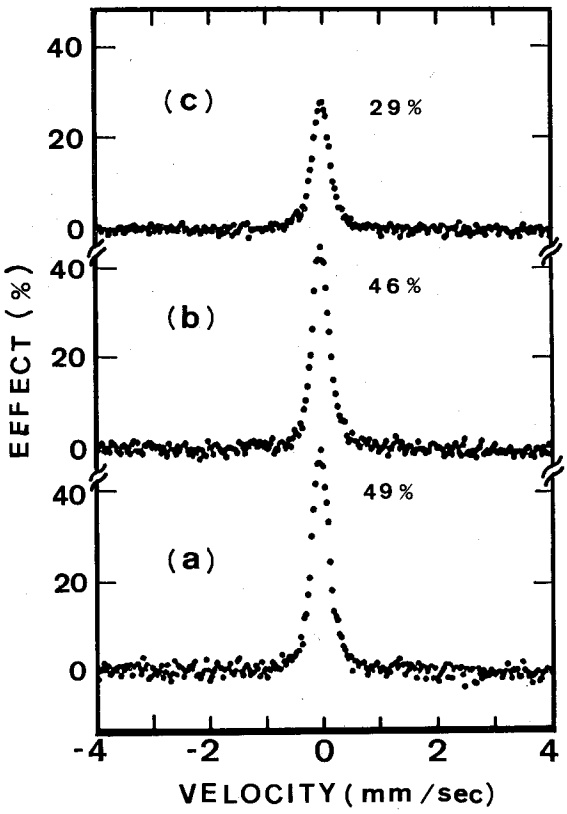

Fig. 8. Mössbauer spectra of a stainless steel of type 310 obtained at various pressures of the counter gas ($He+2\%CH_4$): (a), at 60 Torr; (b), at 200 Torr; (c), at 500 Torr. The measurements were performed at liquid nitrogen temperature (77 K).

6. CONCLUSION

As shown above, the proportional counter with a large sensitive volume (the counter A) is possessed of performances considerably better than other counters previously developed.

1) Energy resolution: The uniform electric field near anode wire, which is due to the large volume, results in better resolution. The energy resolution as good as achieved in the present work (as given by Fig. 1 a) makes possible to perfrom depth-selective Mössbauer spectroscopy, though its accuracy is not so high as that obtained with high-resolution electron spectrometers.

2) S/N ratio of Mössbauer spectrum: The large counter does not always result in a worse S/N ratio of Mössbauer spectra, as long as gas mixtures insenitive to incident photons, e. g., $He+2\%CH_4$ in the present work, are employed as a filling gas. The beam alignment for incident photons becomes easier for larger counters. We actually obtained better S/N ratios with the large counter A than those with small counters

previously used; with such small counters, it is difficult to avoid the collision of a part of incident photons with counter wall.

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